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POLY(DIMETHYLSILOXANES) MODIFIED WITH INORGANIC POLYHEDRA

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Introduction

There has been recent interest in using polyhedral oligomeric silsesquioxanes (POSS) as molecular building blocks in many polymer systems.[1] This interest is driven by significant property enhancements imparted by dispersion of a covalently bound nanosized inorganic particulate into an organic matrix. Most of the work to date has focused on thermoplastic hybrid inorganic/organic polymers[2] derived from either a triol- or a diol-silsesquioxane (Figure 1).

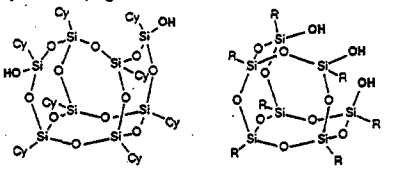

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Figure 1. Two types of incompletely condensed silsesquioxanes used for making hybrid inorganic/organic materials.

Disilanol 1 can be directly condensed with chloro-terminated oligodimethylsiloxane fragments to make alternating "bead type" siloxane copolymers (Figure 2).[1a] The most significant effect of placing a large POSS moiety directly into the main polymer chain is a huge increase in glass transition from −125 °C for normal polydimethylsiloxane (PDMS) to about −65 °C.

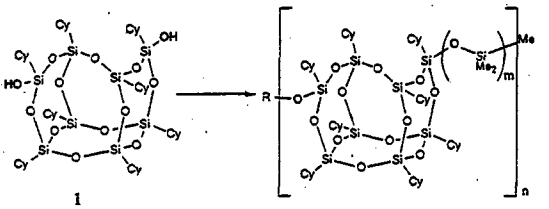

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Figure 2. Disilanol 1 converted into an alternating AB siloxane copolymer.

Trisilanol 2 can be converted into a fully condensed POSS cage containing a single allyl group. The allyl group can be hydrosilated to short chain poly(dimethyl-co-methylhydrido)siloxane fragments to make "pendant type" siloxane copolymers (Figure 3).[3] Large increases in the Tg are again observed, but the effect is slightly less than that seen in the "bead" copolymers.

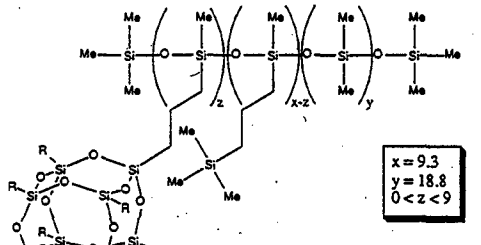

Figure 3. Trisilanol 2 can be derivatized and then appended to short chain poly(dimethyl-co-methylhydrido)siloxanes.

Both "bead" and "pendant" type siloxanes are low degree of polymerization polymers, such that it was not possible to reveal what effect a small weight % of POSS would have on polymer properties. Because a single POSS cage weighs approximately 1000 grams/mole, even a lone POSS cage on a short PDMS chain can take up a significant portion of the weight and/or volume % of the copolymer. To accommodate this disparity in molecular weight between a POSS moiety and a PDMS repeat unit, we decided to graft a POSS-hydride onto high molecular weight PDMS containing variable amounts of latent vinyl functionalities. This then allows us to probe the subtle effects of adding a small weight % of POSS and measure the rheological properties of the resulting polymer. Any observed differences are due entirely to the effect of the POSS on chain dynamics and are independent of small changes in molecular weight.

Experimental

Materials. POSS trisilanols[4], $[R_7Si_7O_9(OH)_3]$ R = cyclopentyl, cyclohexyl or isobutyl, were obtained from Hybrid Plastics. High molecular weight poly(dimethyl-co-methylvinyl)siloxanes were provided by Wacker Silicones Corporation. Tetrachlorosilane and dimethylchlorosilane were purchased from United Chemical Technologies. Tetrahydrofuran was dried by passage through an activated alumina column and triethylamine was distilled from sodium.

Example synthesis of a POSS-hydride, (isobutyl)$_7$Si$_8$O$_{12}$(OSiMe$_2$H), 3c. To a 100 mL round bottomed flask equipped with a stir bar, $iBu_7Si_7O_9(OH)_3$, 2c, (10.00 g, 0.0126 mol), THF (60 mL) and NEt_3 (4.22 g, 0.0417 mol) was added a $SiCl_4$ (2.25 g, 0.0132 mol) THF (10 mL) solution dropwise over 15 minutes. After stirring for two hours, the NEt_3HCl byproduct was filtered off and the solvent removed under reduced pressure. The resulting white powder was extracted with Et_2O (20 mL), refiltered and the solvent removed under reduced pressure to yield 10.45 g (97 %) of $iBu_7Si_8O_{12}(Cl)$. ^{1}H NMR ($CDCl_3$, ppm) 1.89 (mult, 7H), 0.98 (mult, 42H), 0.66 (mult, 14H). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) 25.73, 25.65, 23.89, 23.79, 22.47, 22.41, 22.12 . ^{29}Si{^{1}H} NMR ($CDCl_3$, ppm) -66.9 (s, 3Si), -66.7 (s, 3Si), -67.8 (s, 1Si), -90.7 (s, 1Si). This compound was dissolved in THF (25 mL) and then water (5 mL) was added and the solution stirred overnight. Addition of another 20 mL of water resulted in formation of a phase separated mixture. This was added to 50 mL of CH_3CN to precipitate an 85 % yield (8.71 g) of $iBu_7Si_8O_{12}(OH)$ that was filtered and air dried. ^{1}H NMR ($CDCl_3$, ppm) 1.85 (mult, 7H), 0.95 (mult, 42H), 0.61 (mult, 14H). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) 25.67, 23.86, 23.81, 22.46, 22.41, 22.29. ^{29}Si{^{1}H} NMR ($CDCl_3$, ppm) -66.6 (s, 3Si), -67.7 (s, 4Si), -100.9 (s, 1Si). To a dry hexane (20 mL) solution of monosilanol, $iBu_7Si_8O_{12}(OH)$, (1000 g, 1.20 mmol) and NEt_3 (134 mg, 1.32 mmol) was added $ClSiMe_2H$ (136 mg, 1.44 mmol). After stirring overnight, the NEt_3HCl byproduct was filtered off and the solvent removed under reduced pressure to give POSS-hydride (984mg, 1.10 mmol) in 92 % yield. ^{1}H NMR ($CDCl_3$, ppm) 4.75 (sept, J = 2.5 Hz, 1H), 1.83 (mult, 7H), 0.97 (mult, 42H), 0.62 (mult, 14H), 0.23 (d, J = 2.5 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) 25.71, 23.89, 23.84, 22.51, 22.46, 22.37, 0.20 . ^{29}Si{^{1}H} NMR ($CDCl_3$, ppm) -3.0 (s, 1Si), -66.9 (s, 4Si), -67.9 (s, 3Si), -109.0 (s, 1Si).

Example hydrosilation of poly(dimethyl-co-methylvinyl)siloxane with a POSS-hydride. To make a 5 weight % POSS copolymer, 105 mg of $Cp_7Si_8O_{12}(OSiMe_2H)$, 3a, was added to a well-stirred 60 mL toluene solution containing 2.00 g of poly(dimethyl-co-methylvinyl)siloxane, followed by 1.2 µL of a xylene solution (1.9 % Pt) of Karstedt's catalyst and the solution stirred under nitrogen overnight. The next day, 18 mg of $Me_3SiOSiMe_2H$ was added to react with any remaining vinyl functionality. After stirring overnight the POSS-grafted copolymer was isolated by precipitation into methanol and then dried in a vacuum oven overnight at 50 °C. The yield of product is virtually quantitative. The exact same procedure was followed for producing POSS-PDMS blends except that the platinum catalyst was left out.

Results and Discussion

Synthesis of graftable POSS-hydrides. The readily available POSS-trisilanols **2a,b,c** are easily converted into mono-hydrides useful in hydrosilation based grafting reactions. The trisilanols react with silicontetrachloride in the presence of NEt_3 to produce a fully condensed POSS with a single Si—Cl functionality. This bond can be hydrolized with water to make a POSS-monosilanol, which in turn can be reacted with $ClSiMe_2H$ to form the POSS-hydrides, **3a,b,c** (See Figure 4).

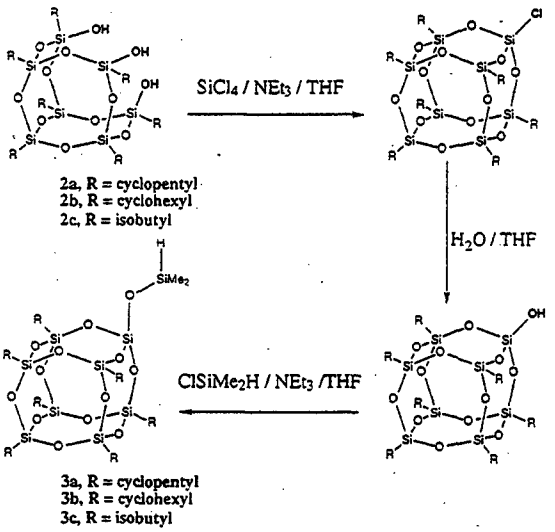

Figure 4. Trisilanols 2a,b,c converted into MonoHydrides 3a,b,c.

Hydrosilation of poly(dimethyl-co-methylvinyl)siloxane with a POSS-hydride. Two high molecular weight vinyl-containing PDMS polymers were chosen for grafting with the POSS-hydrides. One derivative has a degree of polymerization of about 1710 and contains, on average, 7.6 vinyl groups per chain, the other has a degree of polymerization of about 1840 and contains about 66 vinyls per average polymer chain. Completely grafting all of the vinyls on first polymer gives a polymer with only about 5 weight % POSS; the other PDMS can theoretically accommodate over 30 weight % of POSS. The hydrosilations were achieved under dilute reaction conditions in dry toluene under a nitrogen atmosphere using the very reactive Karstedt's catalyst[5] to effect grafting. Following hydrosilation of POSS to the PDMS, all residual vinyl groups were reacted with the small $Me_3SiOSiMe_2H$ hydride to ensure that no post-reaction transformations would occur during analysis of the polymers (Figure 5).

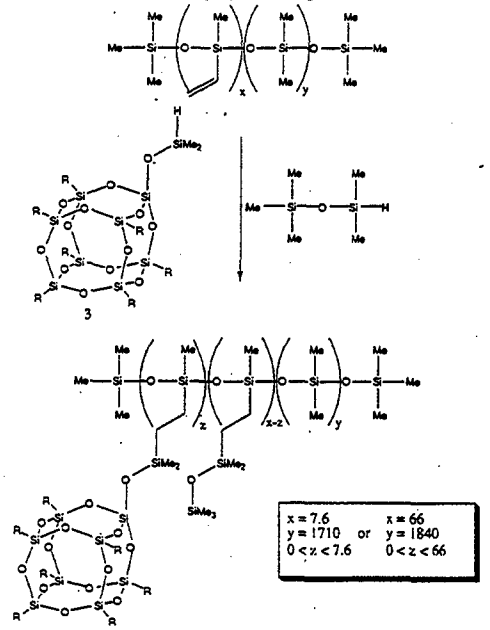

Figure 5. The platinum catalyzed grafting of a POSS-hydride onto high molecular weight vinyl-containing PDMS.

Control reactions were also set up to produce PDMS derivatives grafted only with $Me_3SiOSiMe_2H$ and no POSS. In addition, blends of POSS with the PDMS polymers were made to demonstrate that our observed rheological changes were truly a function of POSS grafting.

Rheological characterization. Preliminary rheological data were collected over a range of temperatures and frequencies. The time temperature superposition principle was applied to the data to extract the characteristic relaxation time of the modified PDMS polymers. Initial results show that blending POSS with the PDMS does not affect this characteristic relaxation time, while grafting about 5 weight % POSS results in an approximately one order of magnitude slowing. Control reactions proved that the observed effects were due to the POSS and not from any post-isolation "curing" of the PDMS being investigated.

Conclusions

The synthesis and effect of covalently tethering a POSS cage to a high molecular weight PDMS backbone over a range of low POSS weight percentages was investigated and compared to just blending equivalent amounts of POSS into PDMS. Significant effects were noted even at POSS loadings as low as 2.5 weight %. Grafting about 5 weight % of $Cp_7Si_8O_{12}(OSiMe_2H)$ onto the PDMS slows the characteristic relaxation time of the polymer by about one order of magnitude. By comparison, blending 5 weight % of POSS with the same PDMS effects no observable change.

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